

The use of micro-FTIR to characterize soil minerals and Boron adsorption

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INTRODUCTION

This study was carried out in an effort to obtain direct structural information of adsorbed boron on the solid surfaces of soil material (clays and oxides). It is necessary to understand the relationship between trace elements and clays at a molecular level to describe and predict interfacial processes controlling trace element retention and release in soils. Our goals for this last proposal period were: 1) to build a spectral library of clay minerals, oxides and boron containing minerals commonly found in California soils. This library would be used in conjunction with x-ray diffraction (XRD) data to determine if micro-Fourier transformed infrared spectroscopy (μ -FTIR) is an appropriate method for identifying clay minerals in soil matrices. 2) Determine which minerals in our spectral library are applicable for studying boron (B) adsorption. Previous studies have found that amorphous $\text{Fe}(\text{OH})_3$ and amorphous $\text{Al}(\text{OH})_3$ are both suitable for B adsorption studies¹. In past work we found a clear spectral differentiation between gibbsite that had been untreated with B and B treated could be detected². These differences are due to specific adsorption of B onto the mineral surfaces. 3) Use a benchtop attenuated total reflectance-Fourier transformed infrared spectroscopy (ATR-FTIR) to examine the coordination of boron adsorption on magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

B has been identified as one of the major trace elements responsible for soil degradation in irrigated areas of the world³. Although B is an essential micronutrient for plants, it can also be toxic at concentrations greater than 1 mg L^{-1} ⁴. In arid and semi-arid regions of the world, where soils are subject to high evapotranspiration rates and poor water quality, they can become enriched in B, becoming an important factor in leaving large areas in the landscape devoid of vegetation.

Boron biogeochemistry is a major factor in managing land reclamation in arid and semi-arid ecosystems. A key factor limiting progress in land management is understanding the processes involved in the retention and slow release of B from the soil inorganic and organic solid-phase. Combining μ -FTIR with ATR-FTIR and XRD, we aim to characterize the composition of the soil matrix and possibly the form and location of B in the soil matrix.

METHODS

Peds (intact pieces of soil) were collected from the Panoche soil series in Fresno County, CA. The Panoche soils are known to be high in B. Yellow and brown deposits were noted throughout the soil profile. The soil peds were air dried at 35°C and impregnated with LR White high grade resin under a vacuum in order to retain soil aggregate structure. The resin was hardened by heating samples at 60°C for 48 hours. The hardened samples were cut into thin sections (0.1-0.2 cm thick) using a diamond edged saw and polished to ensure a smooth surface. The thin sections were then analyzed using μ -FTIR on Beamline 1.4.3. The clay-sized fraction of this soils was also analyzed by XRD to determine clay mineralogy.

Minerals containing B, clay minerals and oxides were obtained for the spectral library. These minerals were analyzed by benchtop FTIR, μ -FTIR and XRD. This provided us with

samples of known characteristics for comparison and were used to create a searchable library in Omnic 5.1.

Boron was also adsorbed onto brucite ($\text{Mg}(\text{OH})_2$) at varying pH's. Samples of 0.3 g MgO were added to 50 mL polypropylene centrifuge tubes containing 25 mL's of 20 ppm B solution, and were shaken for 24 hrs. The suspension pH was adjusted to the desired levels with 1.0 M HCl or NaOH. The supernatant solutions were separated by centrifugation, filtered through a 0.1 mm filter and analyzed for B concentration by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The amount of B adsorbed was calculated as the difference between the total B added and the B that remained in the aqueous solution. The solid material remaining was air dried at room temperature and analyzed by ATR-FTIR and XRD.

RESULTS AND DISCUSSION

μ -FTIR seems to be an appropriate method for the qualitative identification of clay minerals. The spectral library of clay minerals created in Omnic 5.1 was able to correctly identify the clays (originally determined by XRD) in the Panoche soil we collected. The μ -FTIR was useful because we were able to determine the clay mineralogy of specific aggregates in our soil thick-sections. Figure 1 shows the results of a search on the soil matrix. The XRD work done on bulk samples of the Panoche soil gave the same results as the μ -FTIR. The μ -FTIR provides great advantages over common XRD procedures for determining the clay mineralogy which only considers homogenized bulk samples. The drawbacks to this method were that the signal from the hardening resin can interfere with the signal from the samples. Subtracting the resin signal did not remove the interference in all cases.

We found that many of the minerals commonly found in soils are inappropriate for studying B adsorption using FTIR. This is due to the fact that many clay minerals have adsorption bands in the same locations as B adsorption bands. The criteria for selecting minerals appropriate for this study was an absence of bands in the $1600\text{-}1150\text{ cm}^{-1}$ and the $1100\text{-}850\text{ cm}^{-1}$ region. Bands in the $1600\text{-}1150\text{ cm}^{-1}$ region make it difficult to detect trigonally coordinated B ($\text{B}(\text{OH})_3$), and bands in the $1100\text{-}850\text{ cm}^{-1}$ region make it difficult to detect tetrahedrally coordinated B ($\text{B}(\text{OH})_4^-$). Therefore, this criteria excludes most clay minerals from B adsorption studies using FTIR, since most clays have adsorption bands in the $1100\text{-}850\text{ cm}^{-1}$ region, due to the Si-O asymmetric stretching mode.

We found that $\text{Mg}(\text{OH})_2$ may also be promising for B adsorption studies. Magnesium minerals have previously been identified as having appreciable boron-sorption capacities⁵. Since this discovery, no research has investigated this phenomenon in detail.

Samples of $\text{Mg}(\text{OH})_2$ with 1046 mg B kg^{-1} sorbed were analyzed using ATR-FTIR. We could not identify any significant spectral differences between the B treated and untreated $\text{Mg}(\text{OH})_2$. It is possible that the concentration is too low for IR detection or that B is not specifically adsorbing. Another explanation might be that the adsorption bands for trigonal B were masked by a broad adsorption band for carbonate at 1420 cm^{-1} . These solid phase carbonates may have formed in solution and adsorbed, or they could be carbonates formed at the surface of the mineral.

Figure 1 – Results of the Spectral Search for the Panoche Soil

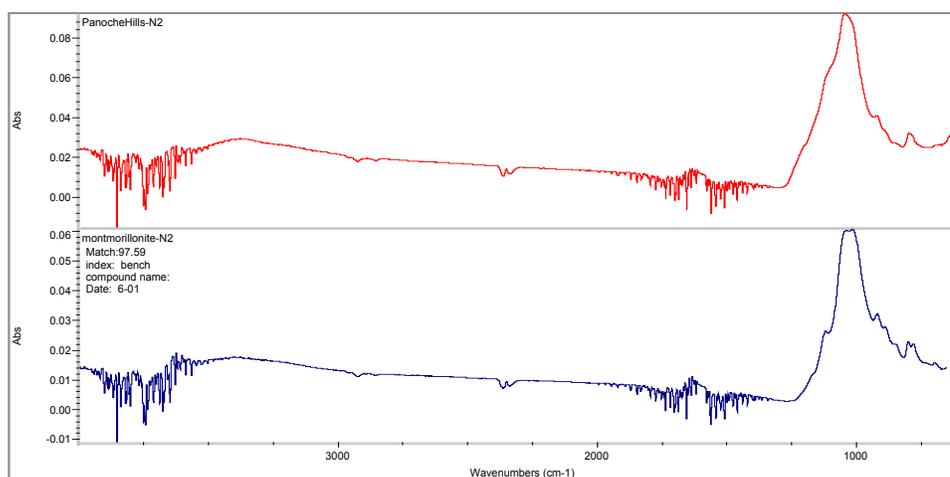


Figure 1 – The top IR spectrum is from the Panoche Soil Series and the bottom spectrum shows the library search results. This match shows that the Panoche soil is predominantly montmorillonite clay.

The μ -FTIR technique has many clear advantages for investigating chemical processes in natural microenvironments as exists in soils. Although our results over that past year were inconclusive, the development of a spectral library will greatly enhance the application of this technique. As an example, given the economic significance of B toxicity in many irrigated systems of the world, a greater understanding of the role of magnesium minerals in controlling the distribution of B in natural systems is crucial for predicting availability, potential toxicity problems, and is essential for evaluating how B rich soils should be managed.

LITERATURE CITED

- ¹Chunming Su and Donald L. Suarez, "Coordination of adsorbed boron: An FTIR spectroscopic study," *Environmental Science and Technology* **29** (2), 302-311 (1995).
- ²P. Fox, H.E. Doner, and S. Pittiglio, "Micro-scale distribution of trace elements in a high boron soil from Kern County, California," (2001).
- ³J. Hren and H. R. Feltz, "Effects of irrigation on the environment of selected areas of the Western United States and implications to world population growth and food production," *Journal of Environmental Management* **52** (4), 353-360 (1998).
- ⁴F. T. Bingham, A.W. Marsh, R. Branson et al., "Reclamation of salt-affected high boron soils in western Kern County," *Hilgardia* **41** (8), 195-211 (1972).
- ⁵J. D. Rhoades, R. D. Ingvalson, and J. T. Hatcher, "Adsorption of boron by ferromagnesian minerals and magnesium hydroxide," *Soil Science Society of America Journal* **34**, 938-941 (1970).

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